PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Aqueous dispersions of Cellulose Glycolic acid or Carboxymethyl Hydroxyethyl cellulose and Water-insoluble coatings Films and Adhesives made therefrom

We, AMERICAN MACHINE & FOUNDRY CO., a corporation organized and existing under the laws of the State of New Jersey, located at 511 Fifth Avenue, New York City, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of preparing aqueous dispersions of cellulose glycolic acid, and of its derivative half ethers with ethylene glycol, known in the art as carboxymethyl hydroxyethyl cellulose, and to stable aqueous dispersions of such compounds, and also to insoluble coatings, sizings, adhesives, and to insoluble films, webs, sheets, and strips produced therefrom.

It is known in the art to employ the alkali metal salts or ammonium salt of cellulose glycolic acid for many purposes. These salts readily dissolve in water to form viscous solutions which have film forming properties and are also useful as thickeners, sizing agents, and stabilizers for a variety of dispersions. For example, sodium cellulose glycolate, which is also known in the trade as the sodium salt of carboxymethylcellulose, "CMC", cellulose gum, and "Carboxymethocel", has been employed in sizing and finishing of textile yarns and fabrics, in grease proofing of paper-board and related products, with detergents to eliminate dirt redeposition, in coating paper to improve physical properties, and in many other compositions, such as paints, pastes, pigments, creams and inks for viscosity adjustment and stabilization.

In spite of their many desirable properties and varied applications, the soluble salts of cellulose glycolic acid have serious limitations, particularly in the form of sheets and webs or when used in sizings, coating and adhesive compositions requiring water insensitivity or insolubility and resistance to deterioration by contact with moisture in the air. For example, sodium cellulose glycolate sheets readily dissolve in water, or become sticky when exposed to high relative humidity in the atmosphere due to moisture absorption. Similar difficulties are encountered with textile yarns, fabrics and the like containing a sizing or coating of sodium cellulose glycolate.

In some instances these difficulties can be overcome by forming a soluble cellulose glycolate into the desired shape, such as a film, thread, filament or coating, and treating the wet shape with a coagulating solution, such as an acid solution or a solution of a precipitating salt, such as aluminium or zirconium salt, thereby forming in situ insoluble cellulose glycolic acid, aluminum cellulose glycolate, or zirconium cellulose glycolate, respectively. Since secondary reaction products are formed through the release of the cation from the cellulose glycolate and the anion from the precipitating salt or acid, and are present in the insolubilized shape together with excess precipitating agent, it is sometimes preferred to remove these by rinsing or washing of the shape. In most cases, the wet shape of soluble cellulose glycolate orignially formed is dried before the insolubilizing agent is applied. Removal of the secondary reaction products and excess precipitating agent is more difficult when the shape is dried before treatment than when it is not dried, but the shape is much less difficult to handle mechanically when dried than when wet. Frequently, however, such treatments are undesirable, impractical or impossible for various reasons. The presence of acid, heavy metal ions, or alkali metal salts may be objectionable and in some cases it is mechanically impractical to remove these by rinsing or washing. Moreover, performing the mechanical operations involved is, in many cases, very complicated and expensive, and thus insolubilization by these techniques increases

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the cost of the product.

Where insolubility of the glycolate used is required, however, insolubilization operations, as above described, have been unavoidable heretofore, since dry insoluble cellulose glycolic acid or its heavy metal or other insoluble salts, as presently known to the art, could not be dispersed in a suitable form and therefore could not be applied or used directly. For example, pure cellulose glycolic acid cannot be dispersed in water without reconversion to a soluble salt, such as by the addition of caustic alkali or ammonia.

The present invention constitutes a solution of this problem because it makes possible the formation of a water dispersion of cellulose glycolic acid or of carboxymethyl hydroxyethyl cellulose which has substantially all of the desirable characteristics and properties of a solution of a soluble salt of cellulose glycolic acid for various applications in addition to the desired water insolubility of the free cellulose glycolic acid. A water dispersion made in accordance with the invention, when used in treating paper, paperboard, textile yarns and textile products, and in the formation of films, webs and strips, results in final products in which the coatings and sizings are insoluble, as are the films, webs, sheets and strips made therefrom. This obviates the necessity of converting in situ the soluble salt of cellulose glycolic acid into insoluble cellulose glycolic acid in a separate operation after impregnation of the textile or formation of a film, and therefore simplifies, expedites and makes less expensive the production of the desired final products, and in some cases, makes it possible to produce products which it is not possible to make by the presently available techniques.

It is an object of this invention, therefore, to provide a novel method for forming aqueous dispersions of cellulose glycolic acid and carboxymethyl hydroxyethyl celluose.

It is a further object of the invention to develop a novel method of forming a dispersion of cellulose glycolic acid or carboxymethyl hydroxyethyl cellulose suitable for use as sizing, thickening, coating and adhesive compositions, and also as a film forming dispersion, by producing a water insoluble form of cellulose glycolic acid in the form of a stable colloidal dispersion which can then be used to produce insoluble, self-supporting continuous sheets and films and also to provide paper, paperboard, textile yarns, and textile fabrics with insoluble coatings, sizings and adhesives.

The invention consists in the novel method of forming a stable aqueous dispersion of cellulose glycolic acid by the acidification of an aqueous solution of a soluble salt of cellulose glycolic acid to precipitate insoluble cellulose glycolic acid and then converting the freshly precipitated, highly hydrated, insoluble cellulose glycolic acid flock resulting therefrom into an aqueous dispersion as described later on which can be used in the formation of water insoluble films, webs and sheets, as a coating or adhesive composition and also for dispersion, stabilization and viscosity adjustment in paints, pigments, and inks.

We have found that cellulose glycolic acid can be precipitated from an aqueous solution of a cellulose glycolate salt, by acidification, in the form of a highly hydrated gelatinous flock, which can be substantially freed of excess precipitating acid and salt by-product without appreciably altering its hydrated gelatinous character. We have also found that the resultant hydrated gelatinous cellulose glycolic acid flock can be readily homogenized or dispersed with or without additional water or additives to form a uniform, stable, smooth, gelatinous dispersion having a creamy or paste-like character. This hydrated gelatinous dispersion can then be formed, as desired, into colorless, transparent, self-supporting, continous sheets and webs and used as coatings, sizings, and adhesives, which after drying, are completely water insoluble, are no longer capable of being rehydrated or swelled to any appreciable extent by water and therefore cannot be redispersed in water.

According to our invention, any soluble salt of cellulose glycolic acid can be employed for precipitating the gelatinous cellulose glycolic acid. For example, the alkali metal salts, such as the sodium, potassium and lithium salts, and the ammonium salt, form aqueous solutions suitable for this process. It is preferred to use the sodium salt since it is available on the market in low, medium and high viscosity grades and also in several degrees of glycolic acid substitution per anhydroglucose unit.

Strong acids, such as chloro-acetic acid, hydrochloric acid or sulfuric acid, are preferred in the acidification step to obtain a pH of 1 to 2 or lower for complete precipitation of the cellulose glycolic acid flock. A considerable excess of precipitating acid is desirable to obtain the gelatinous flock of cellulose glycolic acid in a firm compact form which will withstand the subsequent purification step. The precipitating acid can be poured into the solution of cellulose glycolate salt or the glycolate salt solution may be poured into the acid bath. We have found it advantageous to extrude the cellulose glycolate salt solution through an orifice, for example 1/16" or 1/4" in diameter, into an acid bath. With this technique, the cellulose glycolic acid is obtained in the form of insoluble, gelatinous, continuous, spaghetti-like rods or ropes which are shapes

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well adapted to purification from excess acid and salt by-product.

Time of acidification or contact with the acid bath is not critical as long as the mineral acid has had sufficient time to diffuse thoroughly and uniformly through viscous cellulose glycolate salt solution. With the extrusion technique, using a 1/16" diameter orifice, 15 minutes' acidification time has been found adequate for penetration through the thin spaghetti-like rod of cellulose glycolate salt solution. With rods from larger diameter orifices, such as 1/4", requiring deeper penetration of the acid to accomplish acidification, a period of time as long as four hours may be required, depending, obviously, upon concentration of glycolate solution, concentration of acid and temperature.

Purification of the gelatinous cellulose glycolic acid flock of excess precipitating acid and salt by-product, for example, sodium sulfate or sodium chloride, can be accomplished by several well-known methods. For example, the gelatinous insoluble cellulose glycolic acid flock may be freed from an excess of impurities by diffusion washing in a continuous stream of water. We have found, for example, that gelatinous cellulose glycolic acid in the form of a spaghetti-like rod of 1/16" diameter can be substantially purified of much of the excess sulfuric acid and sodium sulfate by-product by diffusion washing in twenty minutes. In the case of spaghetti-like rods 1/4" in diameter, the time is longer, good results being obtained in approximately two to three hours. Samples of rods or ropes removed during the course of washing and then dispersed in a Waring Blender and then diluted to a definite concentration of cellulose glycolic acid, give colloidal solutions whose viscosity increases as washing progresses and as the precipitating agent and salts are removed.

The purified gelatinous cellulose glycolic acid flock can be homogenized or dispersed to a uniform, stable, smooth, gelatinous, creamy, viscous dispersion or sol by a variety of beaters, agitators and high speed mixers well known in the art, such as colloid mills, ball mills, homogenizers, and Oakes mixers. The viscosity of the resulting dispersion, at any given concentration, can be adjusted within an extremely wide range to obtain almost any desired final viscosity. For example, the viscosity may be raised by increasing the pH such as by the addition of very small amounts of basic materials, e.g., sodium hydroxide, but not in such amounts that a soluble glycolic acid salt is again formed. The viscosity may be lowered by decreasing the pH, such as by the addition of very small amounts of acids. Also, the addition of very small quantities of soluble salts such as aluminum chloride or sodium sulfate, acts to reduce the viscosity. If the washed and drained cellulose glycolic acid rods are permitted to stand for some time, e.g., four hours, before dispersion in a colloid mill, a higher viscosity results. Also, permitting the final dispersion itself to stand for several days at room temperature results in a slight increase in viscosity.

The cellulose glycolic acid dispersion or sol prepared in the above manner can be used as a coating or sizing agent, as an adhesive or for other purposes, such as a stabilizer for dispersions, and a viscosity modifier in paints, pigments or inks, or it can be converted into films and sheets. If the dispersion is to be converted into sheets, this can be done by any suitable well known type of film forming machine, such as a casting roller, to the surface of which the dispersion is applied, or by spraying upon the surface of an endless belt, followed by drying and some baking if a high degree of wet strength is desired. The resulting dry, self-supporting, continuous sheet may then be removed from the belt by a doctor knife and reeled or cut into sheets. The resulting sheet or film is transparent, flexible, water insoluble, and cannot be redispersed in water.

While the strength of films, coatings and sizings, formed from the dispersion described, is good, it is preferred to add a small quantity of an inert and tasteless filler to the dispersion before its use in producing the final desired product. Material such as kaolin, Bentonite, and Fuller's Earth, have produced satisfactory results in increasing the tensile strength of films, coatings and sizings. Aldehydes, such as glyoxal, and salts of certain trivalent and divalent cations such as aluminum chloride, which probably act to form cross linkages and increase the tensile strength in the final product, may also be used. Where better flexibility and prevention of brittleness are desired, it is preferred to add to the dispersion humectants and or plasticizers. Glycerine is a suitable humectant and is well adapted to the method because it also acts as a plasticizer. Obviously, other humectants, such as sorbitol, and ethylene glycol, may be used. The same obtains with respect to other well known types of plasticizers.

One use to which the novel film forming dispersion of the invention can be put is that of forming sheets of reconstituted tobacco wherein it is necessary to insure that the resulting product will have no deleterious effect on the smoking taste of the reconstituted tobacco produced, and the product must have a degree of resistance to steam, moisture and the saliva in the smoker's mouth. A reconstituted tobacco sheet of film, made with the aqueous cellulose gly-

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colic acid dispersion of this invention has these desirable properties. Films produced in accordance with our invention have adequate physical strength and water insolubility.

As noted hereinabove, dispersions of cellulose glycolic acid, made in accordance with the invention can be used satisfactorily as adhesives, especially where a water insoluble adhesive is desirable, as in sealing the longitudinal seam of the paper on a cigarette. Dispersions containing between 1.5 and 2.5% cellulose glycolic acid have proven satisfactory for this purpose, although this range may be varied to suit conditions of use.

The following examples will serve to illustrate our invention in further detail:

EXAMPLE 1

One liter of a solution of 3.75% (high viscosity grade, and 0.70 glycolic acid substitution per 1 anhydroglucose unit) sodium cellulose glycolate was prepared and extruded in the form of a continuous spaghetti-like rod approximately 1/16" diameter into a bath of 4 liters of 22% sulfuric acid and allowed to stand for 20 minutes, during which time the acid penetrated the sodium cellulose glycolate rod to form the gelatinous cellulose glycolic acid. The insoluble spaghetti-like cellulose glycolic acid in the form of gelatinous rods was then removed from the acid bath and washed for 90 minutes in a water bath at a continuous water flow of approximately 5 gallons per minute at a water temperature of 70 F. The washed spaghetti-like rods, substantially free of excess sulfuric acid and sodium sulfate, were removed, drained and colliod milled. The resulting dispersion contained approximately 0.8% cellulose glycolic acid.

EXAMPLE 2

One liter of 4% solution of sodium cellulose glycolate (same type as in Example 1) was prepared and extruded in the form of a continuous rod approximately 1/16 inch in diameter into a bath of 2 liters of 20% hydrochloric acid and allowed to stand for 5 minutes, during which time the hydrochloric acid penetrated the sodium cellulose glycolate and converted it to cellulose glycolic acid. The insoluble spaghetti-like gelatinous cellulose glycolic acid was then removed from the acid bath and washed for 30 minutes in a water bath at a continuous water flow of approximately 5 gallons per minute at a water temperature of 70 F. The washed product was removed, drained, and dispersed in an Oakes Mixer, a type of high speed rotary mixer having a stator and a rotor and means for forcing the material being processed into the range of the stator and rotor. The resulting dispersion contained approximately 2.5% cellulose glycolic acid.

EXAMPLE 3

Same as Example 1, except that 0.4% of kaolin and 0.8% of glycerine, based on the total weight of the finished dispersion, were added to the dispersion after colloid milling and the mixture passed again through a colloid mill to incorporate these additives and form a uniform product.

EXAMPLE 4

Same as Example 1, except that 0.27 grams of a 30% solution of glyoxal in water was added to 100 grams of the finished dispersion after colloid milling, and the mixture was passed again through a colloid mill to form a uniform product.

EXAMPLE 5

One liter of 2.5% solution of sodium cellulose glycolate (medium viscosity grade, containing approximately 0.35 glycolic acid substitution per 1 anhydroglucose unit) was extruded in the form of a continuous rod approximately 1/4 inch in diameter into a bath of 3 liters of 25% sulfuric acid and allowed to stand for 4 hours. The resultant insoluble gelatinous cellulose glycolic acid in the form of spaghetti-like "noodles" was washed, as in Example 1, for three hours. The substantially pure cellulose glycolic acid was processed in a Waring Blender for 2 minutes. The resulting dispersion contained approximately 1.8% cellulose glycolic acid.

EXAMPLE 6

The same as example 4, except that 0.9% of kaolin and 1.8% of glycerine, based on the weight of the finished dispersion in Example 4, were added to the final dispersion and the mixture agitated violently in a Waring Blender to disperse these additives uniformly.

The dispersions produced in accordance with the invention, and as exemplified in the above examples, are suitable for use in coatings and sizings as described hereinabove, and also may be formed directly into self-supporting webs and films. When made into webs and films, a preferred method is to cast the dispersion as a thin, continuous web on a film forming surface, such as an endless travelling stainless steel belt. After casting, the film or web is dried and removed by a suitable device such a doctor blade, well known in the art, in the form of a continuous self-supporting insoluble cellulose glycolic acid web.

In the desesription hereinabove, reference has been made to the use of cellulose glycolic acid and its conversion into stable insoluble aqueous dispersions. The invention is also concerned with the half ethers of cellulose glycolic acid with ethylene glycol known in the art as carboxymethyl hydroxyethyl cellulose, these ethers being available in various degress of substitution per anhydro glucose unit both with respect

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to the ratio of glycolic acid substitution per such unit and the ratio of ethylene glycol half ether substitution per anhydro glucose unit or various comonifications of both these ratios. In general, the techniques described hereinabove for forming aqueous dispersions of cellulose glycolic acid are followed in making aqueous insoluble dispersions of carboxymethyl hydroxyethyl cellulose, which is a material having substantially the same characteristics for the purpose of our invention as cellulose glycolic acid. A satisfactory dispersion of carboxymethyl hydroxyethyl cellulose for use in forming insoluble films, webs and sheets, and also in sizings and coatings, in substantially the same manner as above described dispersions of cellulose glycolic acid can be made as follows:

EXAMPLE 7

Four and one-tenth grams of the dry sodium salt of carboxymethyl hydroxyethyl cellulose were dissolved in sufficient water to form a thick paste. The paste was extruded through a 1/16 inch diameter orifice into 20% sulfuric acid solution and permitted to stand in the acid for two hours. The resulting hardened spaghetti-like threads of insoluble carboxymethyl hydroxyethyl cellulose were removed from the acid, drained, and washed with running water for 20 minutes. The washed threads were then dispersed into a stable aqueous dispersion by processing in a Waring Blender, and the dispersion was cast into a wet web on a plate. The web was dried and the film stripped from the plate. The film was insoluble in water.

We are aware of the Tobacco Act, 1842 (5 and 6 Vict. Cap 93) and make no claim to the use of this invention in contravention of any provisions of that Act. We do, however, expressly make claim to any use of the invention which may now be in contravention of the said Act and which may hereinafter become legal as a result of modification or repeal of the said Act as of the date such use becomes legal.

What we claim is:—

1. Method of forming aqueous dispersions of cellulose glycolic acid or carboxymethyl hydroxyethyl cellulose which comprises acidifying an aqueous solution of a soluble cellulose glycolate salt or soluble salt of carboxymethyl hydroxyethyl cellulose to precipitate gelatinous, cellulose glycolic acid or carboxymethyl hydroxyethyl cellulose flock therefrom, separating said flock from said acidified solution, washing said flock, and dispersing (as hereinbefore described) said flock in water to form said dispersions.

2. Method as claimed in Claim 1 in which the gelatinous flock is dispersed by agitating the flock in water.

3. Method as claimed in Claim 1 and in which the gelatinous flock is dispersed by grinding.

4. Method as claimed in Claim 1, 2 or 3 in which an aqueous viscous solution of sodium cellulose glycolate or the sodium salt of carboxymethyl hydroxyethyl cellulose is extruded into an acid bath to produce ribbons or rods of sodium cellulose glycolate or the sodium salt of carboxymethyl hydroxyethyl cellulose, said ribbons or rods being converted by said acid into gelatinous ribbons or rods of cellulose glycolic acid, or carboxymethyl hydroxyethyl cellulose, which are then separated, washed and dispersed in water.

5. Method as claimed in any of the preceding claims in which a small amount of a filler is added to the so produced dispersion.

6. Method as claimed in Claim 5 in which the filler is kaolin.

7. Method as claimed in any of the preceding claims in which a small quantity of a humectant is added to the so produced dispersion.

8. Method of forming aqueous dispersions of cellulose glycolic acid or carboxymethyl hydroxyethyl cellulose substantially as described with reference to the examples.

9. Webs and films from dispersions of cellulose glycolic acid or carboxymethyl hydroxyethyl cellulose obtained in accordance with the preceding claims which are made by casting the dispersions into a continuous web or film from which moisture is removed to make it self-supporting.

10. A dispersion of cellulose glycolic acid or carboxymethyl hydroxyethyl cellulose whenever obtained by the method claimed in any of Claims 1 to 8.

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EXAMPLE 7

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2. Method as claimed in Claim 1 in which the gelatinous flock is dispersed by agitating the flock in water.

3. Method as claimed in Claim 1 and in which the gelatinous flock is dispersed by grinding.

4. Method as claimed in Claim 1, 2 or 3 in which an aqueous viscous solution of sodium cellulose glycolate or the sodium salt of carboxymethyl hydroxyethyl cellulose is extruded into an acid bath to produce ribbons or rods of sodium cellulose glycolate or the sodium salt of carboxymethyl hydroxyethyl cellulose, said ribbons or rods being converted by said acid into gelatinous ribbons or rods of cellulose glycolic acid, or carboxymethyl hydroxyethyl cellulose, which are then separated, washed and dispersed in water.

5. Method as claimed in any of the preceding claims in which a small amount of a filler is added to the so produced dispersion.

6. Method as claimed in Claim 5 in which the filler is kaolin.

7. Method as claimed in any of the preceding claims in which a small quantity of a humectant is added to the so produced dispersion.

8. Method of forming aqueous dispersions of cellulose glycolic acid or carboxymethyl hydroxyethyl cellulose substantially as described with reference to the examples.

9. Webs and films from dispersions of cellulose glycolic acid or carboxymethyl hydroxyethyl cellulose obtained in accordance with the preceding claims which are made by casting the dispersions into a continuous web or film from which moisture is removed to make it self-supporting.

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